Isomerization of olefins in a two-phase system by homogeneous water-soluble nickel complexes

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Abstract

The first example of nickel catalyzed isomerization of olefins in a two-phase system is reported. Provided that the water-soluble ligand is properly tailored and that the Brönsted acid is suitably selected, the catalytic system appears relatively stable and high catalytic activity can be reached. © 1998 Elsevier Science S.A.

1. Introduction

Liquid/liquid two-phase catalysis is one of the most important current topics of catalysis [1,2]. Indeed, by using a wide range of water-soluble transition metal, this approach has been applied successfully to numerous reactions such as hydroformylation [3,4], hydrogenation [5,6], carbonylation [7–9], oligomerization [10], carbon–carbon coupling [11–13], isomerization [14–17] and its industrial feasibility has been demonstrated by Hœchst in the case of the hydroformylation of propene into butyraldehyde [3,4]. Although one patent claimed the nickel catalyzed addition of hydrogen cyanide to carbon–carbon double bonds [18] and that some water-soluble zerovalent complexes of nickel have been synthesized [19–22], the use of this transition metal in biphasic catalysis has so far been ignored.

In this context, we report herein the first example of alkenes isomerization by water-soluble nickel complexes in a two-phase system. The catalytic system consists of bis(cycloocta-1,5-diene)nickel(0), a water-soluble phosphine and a Brönsted acid dissolved in water or in a water/methanol mixture in order to increase the mass transfer between aqueous and organic layers (Scheme 1).

2. Materials and methods

In a typical experiment, Ni(COD)$_2$ (35 mg), DPPBTS (212 mg-synthesized according to Ref. [23]) and water (5 g) or a mixture of water (5 g) and methanol (5 g), were introduced under nitrogen into a glass tube reactor. After stirring with magnetic bar for 2 h at 80°C, the solution exhibited a orange color and the insoluble Ni(COD)$_2$ has disappeared. This solution was then transferred into a mixture of allylbenzene (750 mg), toluene (6.5 g) and hydrochloric acid (407 mg of a 1.25 N aqueous solution). The medium was stirred at 1000 rpm at 80°C and the reaction was monitored by quantitative gas chromatographic analysis of aliquot samples of the organic layer (CP Sil 5-CB, 25 m × 0.32 mm).

3. Results and discussion

Typical results with allylbenzene as model substrate are reported in Table 1. We first investigated the activities obtained with the sodium salt of trisulfonated triphenylphosphine (TPPTS) as phosphine. The results obtained in water or in hydroalcoholic medium with this common water-soluble phosphine are rather disappointing (entries 1 to 3). Indeed, isomerization occurred only in the presence of Brönsted acids and a total loss of catalytic activity was observed after 5–10 min reaction.

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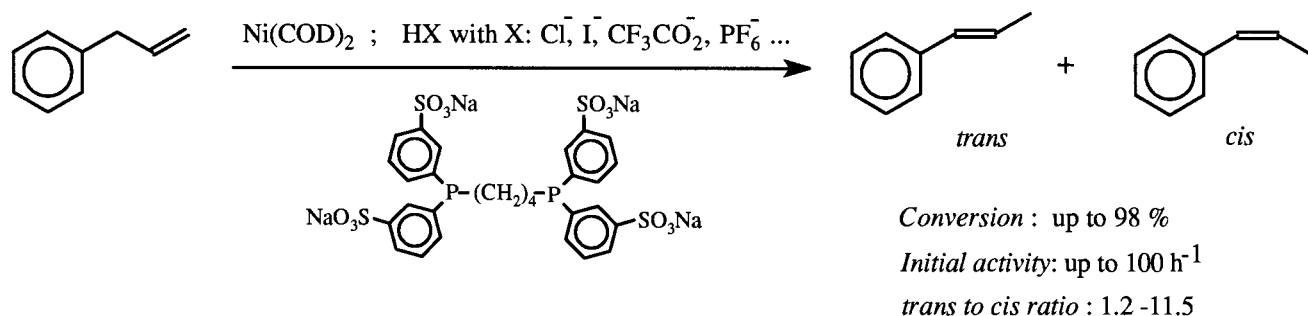
Scheme 1.

For instance, with trifluoroacetic acid, the allylbenzene conversion reached rapidly 7% but stopped after 15 min (entries 2 and 3). This result and the fast color change of the aqueous layer (red-orange to bright green) indicate clearly a catalytic species decay under these experimental conditions.

The above results and the well-know stability of nickel/diphosphine complexes in homogeneous medium [24–26] led us to examine the behavior of a chelating water-soluble phosphine like the sodium salt of tetrasulfonated 1,4-bis(diphenylphosphino)butane (DPPBTS). Interestingly, the catalytic activity was preserved with this ligand and allylbenzene conversion in methanol free medium reached 92% after 48 h (entry 6). It should be noticed that no reaction was observed in the absence of nickel precursor or acid (entries 4 and 5). As expected for weakly water-soluble substrates like allylbenzene, entries 7 and 8 show that the reaction rate is greatly improved by adding methanol to the medium and suggest that the rate determining step is the mass transfer between aqueous and organic layers. Consequently, the behaviour of the nickel/DPPBTS/acid system has been investigated mainly in a biphasic hydroalcoholic medium.

We studied the role of the counteranion on the reaction rate and on the *trans* to *cis* β-methylstyrene ratio (entries 8 to 12). Best results in terms of initial activity have been obtained with acids possessing coordinating anions such hydrogen chloride or hydrogen iodide. Furthermore, in contrast with reactions conducted with non-coordinating anions, the catalytic system appeared more stable with these acids; indicating that the coordinating-anions have a stabilizing effect on the catalytic species. From a stereoselectivity point of view, coordinating anions led to lower *trans* to *cis* β-methylstyrene ratio. As a matter of fact, the *trans*/*cis* ratio reached 1.2 and 5.0 with HPF_6 and HI and, respectively (entries 9 and 11). It must be pointed out that this *trans* to *cis* methylstyrene ratio increases in the course of the reaction whatever the experimental

Table 1
Nickel catalyzed isomerization of allylbenzene in two-phase system[a]

Entry	Catalytic System		Polar layer	Initial TOF (h^{-1})[c]	Allylbenzene conversion		*Trans*/*cis* ratio[e]	
	Phosphane	Acid[b]			1 h	48 h[d]	1 h	48 h
1	TPPTS	–	H_2O	0	0	0	–	–
2	TPPTS	CF_3CO_2H (4)	H_2O	8	7	7	11.5	11.5
3	TPPTS	CF_3CO_2H (4)	H_2O/CH_3OH	7	6	6	11.4	11.4
4	DPPBTS	–	H_2O	0	0	0	–	–
5[g]	–	CF_3CO_2H (4)	H_2O	0	0	0	–	–
6	DPPBTS	CF_3CO_2H (4)	H_2O	6	10	92	5.6	5.6
7	DPPBTS	CF_3CO_2H (4)	H_2O/CH_3OH[f]	33	47	98	6.1	6.2
8	DPPBTS	CF_3CO_2H (4)	H_2O/CH_3OH	71	67	98	5.0	5.4
9	DPPBTS	HPF_6 (4)	H_2O/CH_3OH	63	52	66	5.0	5.1
10	DPPBTS	HBF_4 (4)	H_2O/CH_3OH	52	34	45	4.7	4.8
11	DPPBTS	HI (4)	H_2O/CH_3OH	84	45	98	1.2	1.9
12	DPPBTS	HCl (4)	H_2O/CH_3OH	106	77	99	4.1	5.3
13[g]	–	HCl (4)	H_2O/CH_3OH	0	0	0	–	–

[a]Reaction conditions: $Ni(COD)_2$: 0.13 mmol; phosphine: 0.52 mmol eq. P; allylbenzene: 6.5 mmol; toluene: 6.5 g; Polar layer without cosolvent: water: 5 g; polar phase with cosolvent: water: 5 g; methanol: 5 g; T: 80°C; [b]the acid to nickel ratio is given in brackets. [c]Mol of initially converted allylbenzene per mol of nickel per hour. [d]Unoptimized reaction time. [e]*Trans* to *cis*-β-methylstyrene ratio. [f]Water: 5 g; methanol: 1.7 g.
[g]This control experiment carried out without nickel and DPPBTS proves undoubtedly that the isomerization is not catalyzed by the Brönsted acid.

conditions; indicating that the initial production of the isomers is kinetically controlled. Finally, it is worth mentioning that no addition product with water, hydrochloric or hydroiodic acid has been observed in the experiments.

The nickel/diphosphine/HCl catalytic system is also efficient for the isomerization of other olefins. For instance, hex-1-ene isomerization into hex-2-ene and hex-3-ene can be achieved with an initial turnover frequency of 500 h^{-1}. At hex-1-ene complete conversion, the hex-3-ene to hex-2-ene ratio reached 2.5.

Although no conclusive evidence has been obtained, we believe that the above results can be rationalized if one considers the formation of hydride nickel complexes in the acidic aqueous medium.

By analogy with the behaviour of hydrophobic complexes Ni(PPh$_3$)$_4$ or Ni(DPPB)$_2$ in acidic homogeneous medium [24–26], nickel hydride complexes could be formed by protonation of the water-soluble zerovalent nickel complex Ni(TPPTS)$_3$ or Ni(DPPBTS)$_x$. The resulting cationic hydride could be in equilibrium with ion pair species (A) and covalent species (B) as depicted in Eq. (1). The isomerization of allylbenzene to β-methylstyrene could then be explained from these species via an addition–elimination mechanism, as reported for isomerization conducted in homogeneous medium [27–29]. Moreover, the variation of the catalytic activity and of the stereoselectivity observed with the different anions could be due to a more or less important concentration of these species in the reaction medium.

The poor results obtained with TPPTS could be attributed to the weak stability of the hydride nickel complex of this monodentate phosphine. The degradation of this species would proceed likely through the protonolysis of the hydride–nickel bond [29]. With the chelating tetrasulfonated diphosphine DPPBTS, this side reaction appears considerably reduced and the catalytic activity can be preserved at least for the first 48 h. Further experiments to gain better insight into the stability of the diphosphine/nickel system are currently under way in our laboratory and will not be discussed further here.

Provided that the ligand is properly tailored, this preliminary study proves the ability of nickel water-soluble organometallic complexes to catalyze reactions in aqueous/organic two-phase system. Consequently, further fruitful developments connected with the well-known nickel catalyzed olefin and diene chemistry, especially in cyclodimerisation and oligomerization reactions, can be expected with these complexes in biphasic catalysis.

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